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Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis Polymerization. 1. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length ($n = 2-8$) on the Thermotropic Behavior of the Resulting Polymers.

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Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis
Polymerization. 1. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length
($n = 2-8$) on the Thermotropic Behavior of the Resulting Polymers.

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Abstract

The living ring opening metathesis polymerization of 5-carbo(n -[(4'-methoxy-4-biphenyl)oxy]alkyl)bicyclo[2.2.1]hept-2-ene (**1-n**, $n = 2-8$) by $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{O-}i\text{-Bu})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$) is described. Polymers with degrees of polymerization from 5 to 100 and narrow molecular weight distributions ($M_w/M_n = 1.05\text{-}1.24$) were obtained in high yield. All polymers exhibit an enantiotropic nematic mesophase. Glass transition and isotropization temperatures increase with increasing molecular weight and become independent at approximately 30-50 repeat units. The change in enthalpy of isotropization is relatively independent of molecular weight. Using polymer blends, it was shown that polydispersity has no effect on either the transition temperatures or the temperature range of isotropization. Isotropization alternates in an odd-even manner up to spacer lengths of $n = 6$, and then levels off.

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INTRODUCTION

Living polymerization methods allow one to synthesize polymers with well-defined structures.¹⁻⁵ Although anionic polymerization has been exploited the most, the living nature of the system is often impeded by the presence of polar substituents on the monomer.⁶ Recently, well characterized molybdenum alkylidene complexes of the type $\text{Mo}(\text{CHR})(\text{NAr})(\text{O}-i\text{-Bu})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$, $\text{R} = i\text{-Bu}$ or CMe_2Ph)⁷ have been shown to initiate the living ring opening metathesis polymerization (ROMP) of functionalized norbornenes and norbornadienes.^{5,8-14} Because this initiator tolerates a variety of functional groups, the molecular engineering of polymers with novel structures and functionalities, including side chain liquid crystalline polymers (SCLCPs), should be possible. Related tungsten complexes¹⁵ have also been shown to behave as initiators for certain living polymerization reactions,^{16,17} although tungsten complexes do not appear to tolerate functionalities as well as molybdenum complexes.⁵

SCLCPs have been prepared mainly by radical polymerization of mesogenic acrylates and methacrylates, and by hydrosilating mesogenic olefins with Si-H groups in polysiloxane backbones. Because it is difficult to control both the molecular weight and the polydispersity of the resulting polymers by either of these methods, they are of limited use for determining the influence of molecular weight and molecular weight distribution on the phase behavior of SCLCPs.¹⁸ However, recently both group transfer polymerization and living cationic polymerization of vinyl ethers¹⁹ have been applied successfully to the synthesis of SCLCPs with narrow molecular weight distributions.²⁰⁻²⁸ These reports established the precise relationship between molecular weight and phase behavior, and elucidated the chain length at which the phase transitions no longer vary as additional monomer units are added. Some of these studies also revealed the effect of spacer length on the thermotropic behavior of the SCLCPs.²¹⁻²⁵

Similar data for other types of polymers should help establish trends in structure/property relationships of SCLCPs, and build up knowledge concerning how to prepare novel macromolecules with specific phases and transition temperatures. The polynorbornene backbone should provide some interesting new information. Since polynorbornene has a glass transition

temperature of approximately 40°C, the new SCLCPs should have a flexibility between that of polyvinyl ethers (polymethyl vinyl ether $T_g = -31^\circ\text{C}$) and polyacrylates (polymethylacrylate $T_g = 5^\circ\text{C}$) or polymethacrylates (polymethylmethacrylate $T_g = 100^\circ\text{C}$).²⁹ In this paper we report the living ring opening metathesis polymerization of mesogenic norbornene derivatives using $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{O-}i\text{-Bu})_2$ as the initiator, and describe the influence of spacer length, of molecular weight, and of molecular weight distribution on the phase behavior of the resulting polymers. The norbornene monomer series 5-carbo{n-[(4'-methoxy-4-biphenyl)oxy]alkyl}bicyclo[2.2.1]hept-2-ene (**1-n**) with spacer lengths *n* of two to eight methylenic units will be discussed. The synthesis and thermotropic behavior of compounds with *n* = 9-12 will be presented in a subsequent paper.

RESULTS AND DISCUSSION

Synthesis of monomers

The monomers were synthesized as shown in Scheme I. The first consisted of nucleophilic displacement of the halide of an *n*-haloalkan-1-ol with 4-methoxy-4'-hydroxybiphenyl under basic conditions.³⁰ However, in the case of 4-chlorobutanol, even under very mild conditions the tetrahydrofuran was formed exclusively via intramolecular cyclization. Therefore it was necessary to protect the hydroxy group of 4-chlorobutanol with tetrahydropyran before reaction with 4-methoxy-4'-hydroxybiphenyl. The resulting mesogenic alcohols were then treated with an isomeric mixture of bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride (exo:endo = 1:3). Monomer **1-6** was also synthesized using a higher concentration of the endo isomer (exo:endo=1:9).

All monomers are crystalline and melt into the isotropic state. However less stable crystalline modifications are obtained from the melt than from solution, but the most thermodynamically stable crystalline form also can be obtained from the melt by annealing at the appropriate temperature.

Polymerization of **1-n**

As outlined in Scheme II, *n* equivalents of **1-n** were added to $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{O-}i\text{-Bu})_2$

$\text{Bu})_2^{7,31}$ in THF. After 1 hour at room temperature, benzaldehyde was added to give a benzylidene terminated polymer. The molecular weight of poly(1-*n*) was controlled by varying the molar ratio of the monomer to the initiator ($[\text{M}]/[\text{I}]$). The polymer yields were quantitative in all cases and the polymers were purified by at least one precipitation. The results of polymer characterizations are presented in Table I and Figure 1. A linear relationship is obtained by plotting the number average molecular weight (M_n) of poly(1-4) and poly(1-6) as a function of $[\text{M}]/[\text{I}]$ for ratios up to 100 (Figure 1). Molecular weights were determined by gel permeation chromatography (GPC) versus polystyrene standards. Figure 1b includes the results of polymerization of monomer 1-6 (both ratios of exo:endo isomers). Similar plots were obtained for all other monomers. The fact that these plots are linear, and that the molecular weight distributions ($\text{PDI} = M_w/M_n$) are narrow and independent of molecular weight demonstrates that the polymerizations are living. However, the lines do not extrapolate to the origin, indicating that the true molecular weights differ slightly from those determined by comparison with polystyrene standards. The molecular weights of the 100mers tend to deviate more from theory than shorter polymers because of increased sensitivity of the catalytic intermediates to trace impurities, to experimental error in measuring small amounts of catalyst, and perhaps also to slow reaction of catalytic intermediates with the ester functionality. Although 100mers of 1-*n* ($n = 6,8$) sometimes showed a small double molecular weight peak by GPC analysis, the PDIs are still lower than 1.24. The GPC traces of poly(1-6) and poly(1-7) are presented in Figure 2, along with GPC traces of some polymer blends (*vide infra*).

Proton NMR spectra of poly(1-*n*) showed broad resonances at 5.2-5.6 ppm for the olefinic protons and broad resonances at 1.6-2.0 and 2.2-3.0 ppm for protons of the five-membered ring, consistent with the ring-opened structure. We presume the detailed polymer structure is complex, consisting of cis and trans double bonds, and head-to-head, head-to-tail and tail-to-tail arrangements of the repeat units.^{32,33} In contrast, the resonances due to the aromatic protons of the mesogenic biphenyl group are relatively sharp.

Thermal characterization of polymers

Poly(1-*n*) was characterized by a combination of differential scanning calorimetry (DSC) and thermal polarized optical microscopy. The first and subsequent DSC heating scans were essentially identical, and all heating and cooling scans were completely reproducible. Figures 3 and 4 show the second heating and first cooling scans of poly(1-6) and poly(1-7) with theoretical degrees of polymerization of approximately 5 to 100; they are typical of the scans obtained for polymers with other spacer lengths. The complete thermal transitions from the second heating and first cooling scans of all polymers are summarized in Table I.

With the exception of oligomers of 1-5, poly(1-*n*) (*n* = 2-8) displays only an enantiotropic nematic mesophase over the entire range of molecular weights and flexible spacer lengths. The textures observed by polarized optical microscopy and the small enthalpy changes are characteristic of nematic mesophases. Figure 5 is a representative polarized optical micrograph showing the schlieren texture of poly(1-4). The presence of a nematic mesophase contrasts with the crystalline nature of the corresponding monomers. Although stabilization of a liquid crystalline mesophase by polymerization is traditionally explained as a "polymer effect", the structures of the norbornene monomer and the resulting polymer repeat unit are substantially different and therefore are not directly comparable.

Poly(1-5) containing at least 20 repeat units also displays an enantiotropic nematic mesophase. However, the nematic mesophase of the two lower molecular weight oligomers is monotropic and observable only on cooling, while a melting point is observed on heating, in addition to the glass transition. As shown in Figure 6, a transition ascribable to recrystallization overlaps with one ascribable to vitrification of the 9mer on cooling. Therefore, the sample undergoes continued recrystallization upon heating through the glass transition, followed by melting. The same is true of the 12mer except that recrystallization is not detected on cooling. However, the fact that the enthalpy of the recrystallization endotherm is only 60% of that of melting demonstrates that some recrystallization did take place on cooling. Crystallization evidently is suppressed below the glass transition temperature at higher molecular weights. We cannot explain

why only the oligomers of the 5-spacer are crystalline.

The phase transition temperatures of each polymer obtained on heating are plotted in Figure 7 as a function of the degree of polymerization obtained by GPC analysis. Regardless of the length of the spacer, the glass transition and isotropization temperatures of all polymers become independent of molecular weight at approximately 30-50 repeat units. These results are analogous to those reported for mesogenic polysiloxanes (DP~12),³⁴ polyvinyl ethers (DP~10-20),²⁰⁻²⁵ and polyacrylates (DP~12-40)^{35,36} and polymethacrylates (DP~12).¹⁹ There are a few examples using less well-defined systems which report unexpectedly high values of a few hundred repeat units.³⁷⁻³⁹

Table I also lists the change in enthalpy of isotropization for all polymers at each molecular weight and all spacer lengths. Because the enthalpy change of the nematic-isotropic transition is so small and therefore subject to experimental error, the data are scattered as a function of molecular weight. In general, however, the enthalpy change is relatively independent of molecular weight, except for the lowest degree of polymerization.

The peak width of transitions involving liquid crystalline mesophases as a function of molecular weight is also of interest. Because the transition temperatures of oligomers depend on the chain length, we might expect that the peak widths of oligomers should be broader than those of high molecular weight polymers with the same polydispersity. In addition, polydisperse oligomers would then be expected to exhibit broader peaks than essentially monodisperse oligomers and polymers. This trend has been observed for both main chain LCPs,⁴⁰ and for some mesogenic polysiloxanes⁴¹ and polyvinyl ethers.²¹⁻²⁵ However, this argument assumes that each chain length melts independently, even when the different chain lengths are isomorphous. An alternative argument is that since the rate of formation of each phase decreases with increasing molecular weight due to increasing viscosity, transitions of higher molecular weight polymers should be slower than those of lower molecular weight polymers, with the result that the transition occurs over a broader temperature range. Indeed, the peak width of isotropization also has been observed to increase with increasing molecular weight over the range of molecular weights where

the transition temperatures are independent of molecular weight.¹⁹

With the exception of the poly(1-6) 145mer, it appears that the isotropization transitions plotted in Figure 3 may become slightly sharper as molecular weight increases. The peak width also can be qualitatively observed by polarized optical microscopy, since it corresponds to the amount of biphasic material (anisotropic and isotropic) present at the transition. In order to determine whether or not polydispersity affects the sharpness of the nematic-isotropic transition of these polymers, we prepared the multimodal blend of poly(1-6) shown in Figure 2a using low PDI 9, 16, 57 and 145mers in a ratio of 15:15:15:55. The resulting blend has a number average molecular weight of 9741 ($DP = 23$) and a polydispersity of 2.5. Even this multimodal sample undergoes a sharp transition from the nematic to the isotropic state (Figure 4), and the glass transition and isotropization temperatures of this blend correspond to those of a monomodal/monodisperse 23mer (Table I).

We also prepared the bimodal blend of the 6 and 78mers of poly(1-7) shown in Figure 2b. This blend has a number average degree of polymerization of 22 and a polydispersity of 4.78. The nematic-isotropic transition of this extremely polydisperse sample is also sharp (Figure 4), and the transition temperatures again correspond to those of a monodisperse 17mer (Table I). Therefore, the peak width is *not* affected by polydispersity if the component polymers are isomorphic over the temperature range at which the transition occurs.

As discussed earlier, the spacer length does not affect the molecular weight at which the phase transitions become independent of molecular weight. However, the spacer length does affect the temperature of the transitions. The transition temperatures determined on heating are plotted in Figure 8 as a function of the number of methylenic units in the flexible spacer, including poly(1- n) with $n = 9-12$.⁴² In order to avoid errors ascribable to the theoretical and/or experimentally determined molecular weights, the transition temperatures are plotted only for the 50mers and 100mers, since the temperatures of these transitions are independent of molecular weight. The glass transition temperature decreases rapidly with increasing spacer length as a consequence of decreased packing density of the chains. Those compounds with $n \geq 9$ exhibit side

chain crystallization; melting/crystallization overlaps T_g when $n = 10-12$. In general, the isotropization temperatures decrease slightly as the spacer length increases, with an odd-even alternation. This alternation is observable only for spacer lengths up to $n = 6$. Polymers that contain even spacers display higher isotropization temperatures than those that contain the odd spacers.

Since the glass transition temperatures decrease rapidly with increasing spacer length while isotropization decreases only slightly, the temperature window of the mesophase is broader for the longer spacers. Figure 7 also demonstrates that the temperature window broadens as spacer length and molecular weight increase. This is generally true for SCLCPs, except that an increase in the isotropization temperature with increasing spacer length may also contribute to stabilization of the mesophase.^{21-25,43-45}

With SCLCPs, there has been some discrepancy as to whether even or odd member spacers result in higher isotropization temperatures. This discrepancy was resolved for polysiloxanes, polyacrylates, and polymethacrylates by considering the total number of atoms between the backbone and mesogen as part of the "spacer", including the interconnecting units.¹⁸ In this case, "even spacer" lengths result in higher smectic-isotropic transition temperatures because they place the mesogen perpendicular to, rather than at an angle to the polymer backbone. Consequently the anisotropy and linearity of the mesogenic side chains are enhanced, and the formation of layers favored. In contrast, the nematic-isotropic transition temperatures of polyvinyl ethers containing 4-cyano-4'-biphenyloxy mesogens and short spacers are higher for the "odd spacers" than for the "even spacers".

As shown in Scheme III, similar arguments can be applied to this mesogenic polynorbornene system. However, in order to compare it with the above acyclic polymer backbones, the substituted carbon atom of the cyclopentane ring may also be considered as part of the "spacer". If this is so, then "even spacers" are more linear and anisotropic, and our data agree with those obtained for polysiloxanes, polyacrylates, and polymethacrylates. On the other hand, if the substituted carbon of the cyclopentane ring is not considered part of the spacer, then "odd

spacer" lengths are more anisotropic and should have the higher transition temperatures corresponding to the polyvinyl ethers. Therefore, these results do not resolve the confusion; results from additional well defined systems exhibiting nematic-isotropic and smectic-isotropic transitions will be required. However, the relative anisotropy and placement of the mesogen relative to the backbone may not dictate the stability of nematic mesophases, or the orientation of the backbone and mesogen may not be comparable in these two polyvinyl ether and polynorbornene systems. That is, since there are three nematic mesophases possible in SCLCPs which are defined by the relative orientations of the mesogenic side chain and polymer backbone,⁴⁶ the nematic mesophases of the polyvinyl ether system and this polynorbornene system may be different and therefore not comparable.

CONCLUSIONS

5-Carbo{n-[(4'-methoxy-4-biphenyl)oxy]alkyl}bicyclo[2.2.1]hept-2-enes with $n = 2-8$ were polymerized by ring opening metathesis polymerization in a living manner to provide a complete series of well defined SCLCPs with systematically varying molecular weights. All polymers exhibit an enantiotropic nematic mesophase which is stabilized by both increasing molecular weight and increasing spacer length. Because of the simplicity of the mesomorphic behavior of this system, it was possible to determine the effect of polydispersity on the transition temperatures by blending monodisperse polymers. The isotropization temperature of polydisperse and multimodal blends corresponds to that predicted by the number average molecular weight. In addition, the range over which this transition occurs is not influenced by the polydispersity. In this system, the transitions become independent of molecular weight when chains contain 30-50 repeat units, and polymers with an odd number of methylenic units in the spacer display higher transition temperatures than those with an even number. This alternation vanishes when the spacer length is greater than $n = 6$.

EXPERIMENTAL SECTION

Materials and Methods. All polymers were prepared in THF under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran was vacuum transferred from sodium benzophenone ketyl just before use. Diethyl ether and THF used for monomer synthesis were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane used for purification of monomers was distilled from calcium hydride under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. 4,4'-Dihydroxybiphenyl (97%), 2-chloro-1-ethanol (99%), 3-chloro-1-propanol (98%), 6-chloro-1-hexanol (97%), 7-bromo-1-heptanol (95%), and 8-bromo-1-octanol (95%) were used as received from Aldrich. 4-Chloro-1-butanol (Aldrich, 85%) was washed with aq NaHCO₃, dried with MgSO₄, and distilled. 5-Chloro-1-pentanol (95%) was used as received from Lancaster Synth. Inc. 2-Norbornene-5-carboxylic acid chloride (exo/endo = 1/3)⁴⁷ and 4'-methoxy-4-hydroxybiphenyl⁴⁸ were prepared as described in the literature. Endo-2-norbornene-5-carboxylic acid was synthesized by hydrolysis of the corresponding endo-methyl ester obtained by the Lewis acid catalyzed Diels-Alder addition of cyclopentadiene and methylacrylate.⁴⁹ Endo-2-norbornene-5-carboxylic acid chloride was prepared by treatment of the carboxylic acid with PCl₅ under standard conditions. All other reagents and solvents were commercially available and used as received.

The catalyst was synthesized in four steps from [NH₄][Mo₂O₇];³¹ the intermediates are Mo(NAr)₂Cl₂(dimethoxyethane), Mo(NAr)₂(CH₂-t-Bu)₂, and Mo(CH-t-Bu)(NAr)₂(triflate)₂(dimethoxyethane).⁷ It is very important to remove all ArNH₃OTf from Mo(CH-t-Bu)(NAr)₂(triflate)₂(dme) before adding lithium t-butoxide. All steps must be carried out under a dinitrogen atmosphere and the catalyst must be stored and used under dinitrogen or other inert gas in the absence of water and other potentially reactive protic impurities in the monomer (e.g., carboxylic acid or alcohol). The catalyst used in these studies was stored as a solid at -40 °C under dinitrogen.

Polymer blends were prepared by coprecipitation in methanol of the appropriate amount of

each component from THF (0.05 g/mL); the yield of the blend of poly(1-6) was 76%, while the yield of poly(1-7) was 77%.

300 MHz ^1H NMR spectra were recorded on a Varian XL-300 spectrometer. All spectra were recorded in CDCl_3 with TMS as internal standard. Obvious multiplicities and routine coupling constants are usually not listed. Molecular weight was determined by gel permeation chromatography (GPC) at room temperature using a set of Shodex KF802.5, 803, 804, 805, 800P columns ($700, 2 \times 10^3, 2 \times 10^4, 1 \times 10^5$ Å, and a precolumn, respectively), a Knauer differential refractometer, and a Spectroflow 757 absorbance detector set at 300 nm on 0.1-0.3 % (w/v) samples in THF. GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03×10^6 MW. A Perkin Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions which were read as the maxima and minima of the endothermic or exothermic peaks, respectively. All heating and cooling rates were $20^\circ\text{C}/\text{min}$. Glass transition temperatures (T_g 's) were assumed to be the temperature at the middle of the change in the heat capacity. All second and subsequent heating scans were identical. A Nikon optical polarized microscope (magnification 160x) equipped with a Mettler FP82 hot stage and a Mettler FP800 central processor was used to observe the thermal transitions and to analyze anisotropic textures.

Synthesis of n -[(4'-methoxy-4-biphenyl)oxy]alkyl-1-ol ($n = 2-8$). All of the compounds except $n = 4$ were synthesized by a modified literature procedure³⁰ as in the following example. 5-Chloro-1-pentanol (3.8 g, 0.031 mol) was added to a solution of 4'-methoxy-4-hydroxybiphenyl (6 g, 0.03 mol) and NaOH (1.2 g, 0.03 mol) in ethanol (50 mL) and water (3 mL). After stirring at reflux for 24 h, the reaction mixture was poured into water and the precipitated product was filtered and washed with 150 mL of 10% aq NaOH and water. Recrystallization from ethanol yielded 3.9 g (45%) of colorless crystals. Higher yields (>80%) were obtained using bromoalcohols.

2-[(4'-Methoxy-4-biphenyl)oxy]ethanol. ^1H NMR δ 2.10 (t, 1H, -OH), 3.90 (s, 3H, CH_3O -), 4.05 (m, 2H, $-\text{CH}_2\text{OH}$), 4.18 (dd, 2H, $-\text{CH}_2\text{OAr}$), 7.01 (dd, 4, H_{aryl}), 7.53 (dd, 4,

H_{aryl}).

3-[(4'-Methoxy-4-biphenyl)oxy]-1-propanol. ¹H NMR δ 1.72 (t, 1H, -OH), 2.03 (q, 2H, -CH₂CH₂OH), 3.80 (s, 3H, CH₃O-), 3.86 (dt, 2H, -CH₂OH), 4.13 (t, 2H, -CH₂OAr), 6.92 (dd, 4, H_{aryl}), 7.44 (dd, 4, H_{aryl}).

4-[(4'-Methoxy-4-biphenyl)oxy]-1-butanol was synthesized from the tetrahydropyranyl ether of 4-chloro-1-butanol prepared by a standard procedure.⁵⁰ The chloroether was reacted with 4'-methoxy-4-hydroxybiphenyl and the resulting substituted tetrahydropyranyl ether was hydrolyzed without separation: ¹H NMR δ 1.56 (br t, 1H, -OH), 1.85 (m, 2H, -CH₂CH₂OAr), 1.97 (m, 2H, -CH₂CH₂OH), 3.80 (dt, 2H, -CH₂OH), 3.90 (s, 3H, CH₃O-), 4.10 (t, 2H, -CH₂OAr), 7.00 (dd, 4, H_{aryl}), 7.52 (dd, 4, H_{aryl}).

n-[(4'-Methoxy-4-biphenyl)oxy]-1-alkanol. The ¹H NMR spectra of the n-[(4'-methoxy-4-biphenyl)oxy]-1-alkanols, $n \geq 5$, are identical: δ 1.25 (t, 1H, -OH), 1.3-1.7 (m, 2[n-3]H, -[CH₂]_{n-3}-), 1.83 (q, 2H, -CH₂CH₂OAr), 3.65 (q, 2H, -CH₂OH), 3.85 (s, 3H, CH₃O-), 4.00 (t, 2H, -CH₂OAr), 6.96 (dd, 4, H_{aryl}), 7.46 (dd, 4, H_{aryl}).

Synthesis of 5-carbo{n-[(4'-methoxy-4-biphenyl)oxy]alkyl}-bicyclo[2.2.1]hept-2-enes (1-n, n = 2-8). The 1-n monomers were prepared in 70-80% yield as in the following example. A solution of 2-norbornene-5-carboxylic acid chloride (1.56 g, 9.96 mmol) in THF (5 mL) was added dropwise to a refluxing slurry of 7-[(4'-methoxy-4-biphenyl)oxy]-1-heptanol (3.0 g, 9.54 mmol) and triethylamine (1.01 g, 9.98 mmol) in THF (40mL). The solution was refluxed and stirred for 24 h. The mixture was cooled and the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform and the solution was washed with aqueous K₂CO₃ and water, and then dried over anhydrous MgSO₄. Concentration of the filtered chloroform solution yielded 3.31 g (80%) of 1-7.

All monomers were purified by column chromatography using Al₂O₃ as the stationary phase and THF as eluent, followed by at least two recrystallizations in the drybox from ether, ether:pentane or ether:methylenechloride. The monomers were recrystallized until no improvement was seen in the polydispersity of polymers prepared using 100 equiv of monomer: ¹H NMR

resonances at δ 1.32 (d), 1.5 (m), 1.6 (d), 1.94 (m), 2.31 (dd), 2.98 (br s), 3.06 (td), 3.12 (br s) and 3.30 (br s) are due to the non-olefinic norbornene protons of both isomers; 5.95 (dd) and 6.21 (dd) are due to the endo olefinic protons, and 6.15 (m) is due to the exo olefinic protons; 1.2-2.0 (m, $2[n-2]H$, $-[CH_2]_{n-2}-$), 3.86 (s, 3H, $-OCH_3$), 4.07 (t, 2H, $-CH_2OAr$), 4.18 (m, 2H, $-CH_2OOC-$). Melting points (by DSC) are: **1-2** 94°C; **1-3** 91°C; **1-4** 77°C; **1-5** 98°C; **1-6** 72°C; **1-7** 80°C; **1-8** 60°C.

Polymerization procedure. A solution of $Mo(CH-t-Bu)(NAr)(O-t-Bu)_2$ (0.2 mL, 0.0205 mol/L) in THF was added in one portion to a rapidly stirred solution of monomer (3 mL, 0.137 mol/L, 100 equiv) in THF and the mixture was then stirred for 1h. The polymerization was quenched by adding 20 μ L of benzaldehyde (0.19 mmol). After 30 min, the solution was added dropwise to methanol (~50 mL) and the precipitated polymer was isolated by centrifugation, washed with methanol, and dried in vacuo. In all cases, polymer yields were more than 90% and GPC analyses showed no traces of monomer. Further purification of samples by reprecipitation had no effect on their thermotropic behavior. When 20 equiv or less of monomer was used, the catalyst concentration was adjusted to 0.205 mol/L: 1H -NMR δ 1.0 (m, terminal $t-Bu$), 1.2-2.2 (br), 2.2-3.2 (br), 3.85 (s, $-OCH_3$), 4.07 (br, $-CH_2OAr$), 4.26 (br, $-CH_2OOC-$), 5.15-5.55 (br, olefinic H), 6.97 (br d, H_{aryl}), 7.51 (br d, H_{aryl}).

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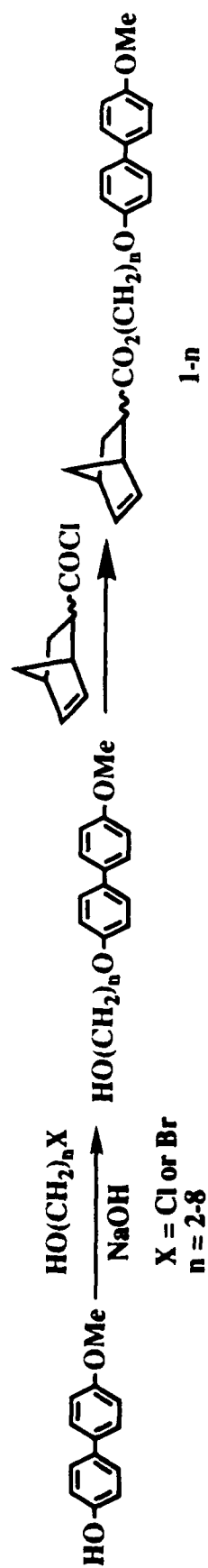
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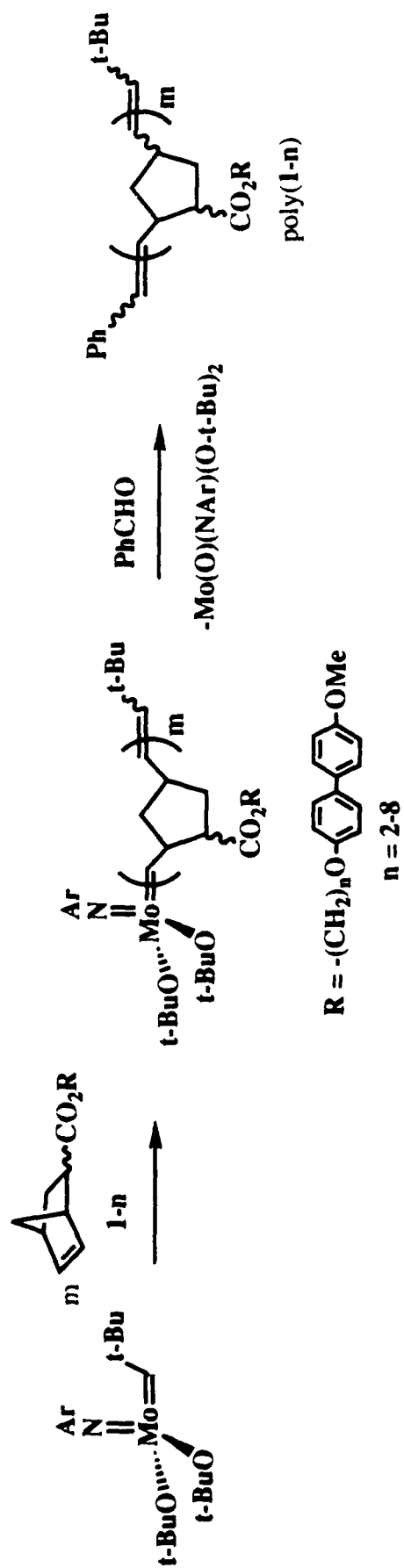
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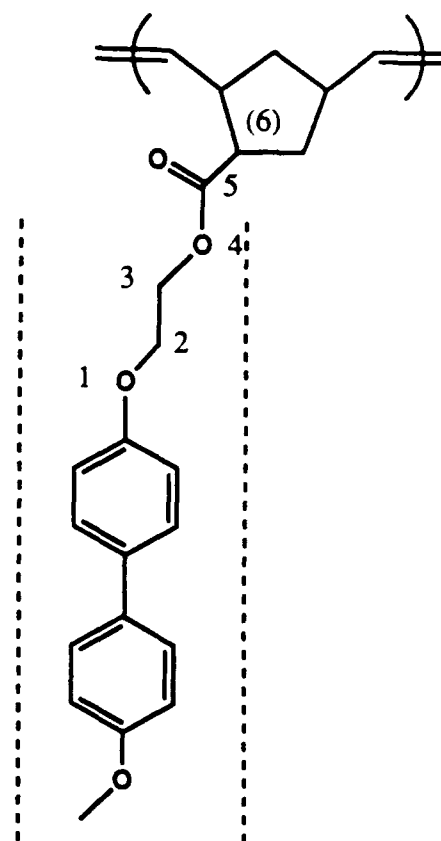
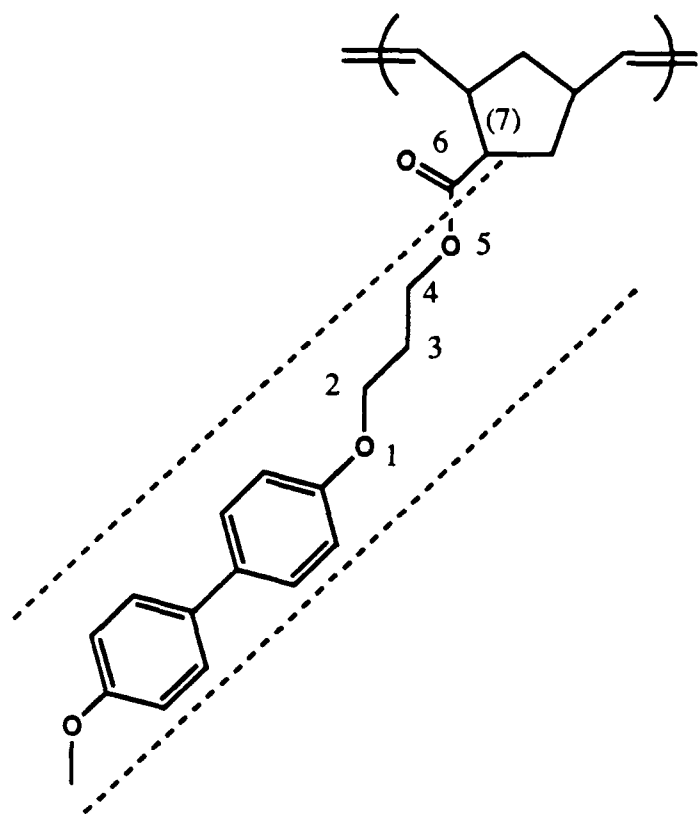
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Scheme 1



Scheme II



Scheme III

Table I

Polymerization of 1-n and Characterization of the Resulting Polymers

[1-n]/[Mo] monomer (mol/mol)	Theor.		GPC		phase transition(°C)		and corresponding enthalpy changes(kJ/mru) ^a
	Mn	DP	Mn	DP	heating	cooling	
1-2	100	36444	37306	1.05	102	g 74 n 93 (0.53) i	i 80 (0.59) n 74 g
1-2	50	18555	15225	1.07	42	g 71 n 91 (0.62) i	i 77 (0.39) n 64 g
1-2	20	7289	6799	1.09	19	g 69 n 87 (0.76) i	i 76 (0.55) n 64 g
1-2	10	3644	4310	1.14	12	g 63 n 78 (0.29) i	i 66 (0.40) n 55 g
1-2	5	1822	2782	1.14	8	g 57 n 69 (0.08) i	i 57 (0.27) n 50 g
1-3	100	35341	43993	1.20	125	g 61 n 88 (0.51) i	i 80 (0.56) n 55 g
1-3	50	17671	20172	1.08	57	g 61 n 86 (0.56) i	i 78 (0.62) n 54 g
1-3	20	7068	7633	1.12	22	g 57 n 79 (0.61) i	i 72 (0.53) n 52 g
1-3	10	3534	4224	1.13	12	g 53 n 71 (0.48) i	i 63 (0.58) n 46 g
1-3	5	1767	2663	1.16	8	g 48 n 62 (0.22) i	i 51 (0.25) n 41 g
1-4	100	39249	52857	1.05	150	g 51 n 96 (1.13) i	i 91 (1.24) n 45 g
1-4	50	19625	21800	1.05	62	g 50 n 93 (1.10) i	i 88 (1.13) n 43 g
1-4	20	7850	9376	1.09	27	g 43 n 85 (0.95) i	i 80 (0.98) n 37 g
1-4	10	3925	5804	1.11	16	g 42 n 78 (0.90) i	i 73 (0.94) n 34 g
1-4	5	1963	3755	1.14	11	g 34 n 67 (0.75) i	i 61 (0.75) n 27 g

(Continuation of Table I)

1-5	100	40552	61247	1.12	151	g 44 n 88 (1.34) i	i 82 (1.27) n 37 g
1-5	50	20326	26386	1.06	65	g 43 n 87 (1.39) i	i 81 (1.27) n 37 g
1-5	20	8110	8185	1.11	20	g 40 n 80 (1.16) i	i 74 (1.07) n 34 g
1-5	10	4055	4963	1.12	12	g 51 k 74 (-3.64) k 90 (5.93) i	i 78 (1.10) n 43 g
1-5	5	2033	3490	1.12	9	g 46 k 66 (-1.92) k 87 (6.85) i	i 65 n 59 k (3.08) ^c g
1-6	100	42055	61022	1.17 ^d	145	g 43 n 95 (1.43) i	i 88 (1.47) n 37 g
1-6	50	21028	24067	1.16	57	g 42 n 93 (1.42) i	i 88 (1.47) n 35 g
1-6 ^e	50	21028	23383	1.13	56	g 38 n 92 (1.39) i	i 86 (1.48) n 29 g
1-6	20	8411	6739	1.16	16	g 35 n 87 (1.43) i	i 81 (1.48) n 28 g
1-6 ^e	20	8411	9690	1.20	23	g 34 n 86 (1.23) i	i 79 (1.21) n 26 g
1-6	15	6308	5165	1.17	12	g 33 n 84 (1.17) i	i 77 (1.31) n 26 g
1-6	10	4206	3962	1.16	9	g 31 n 80 (1.31) i	i 74 (1.15) n 25 g
1-6	5	2103	2663	1.20	6	g 28 n 72 (1.19) i	i 66 (0.92) n 22 g
1-6	blend ^f		9741	2.50	23	g 37 n 89 (1.41) i	i 83 (1.55) n 30 g
1-7	100	43457	34089	1.17	78	g 38 n 95 (2.12) i	i 89 (1.90) n 30 g
1-7	50	21729	15326	1.05	35	g 36 n 93 (1.94) i	i 86 (1.88) n 28 g
1-7	20	8961	7257	1.09	17	g 31 n 85 (1.60) i	i 79 (1.73) n 23 g
1-7	10	4346	4254	1.11	10	g 28 n 79 (1.28) i	i 73 (1.63) n 20 g
1-7	5	2173	2817	1.16	6	g 24 n 71 (1.18) i	i 64 (1.30) n 17 g
1-7	blend ^f		7546	4.78	17	g 28 n 83 (1.63) i	i 76 (1.81) n 21 g

(Continuation of Table I)

1-8	100	44861	46386	1.23d	103	g 30 n 91 (1.55) i	i 83 (1.76) n 21 g
1-8	50	22430	17498	1.11	39	g 27 n 87 (1.83) i	i 82 (1.75) n 21 g
1-8	20	8972	6846	1.12	15	g 26 n 84 (1.60) i	i 78 (1.67) n 19 g
1-8	10	4486	4082	1.14	9	g 23 n 79 (1.48) i	i 73 (1.75) n 17 g
1-8	5	2243	2791	1.17	6	g 20 n 73 (1.41) i	i 67 (1.53) n 13 g

a Data from second heating and first cooling scans. b Monotropic. c Overlapped with previous transition. d A small double molecular weight peak was present. e Exo/endo=10:90. f See text.

Figure Captions

Figure 1. Plots of the number average molecular weight (M_n) and the polydispersity ($PDI = M_w/M_n$) of (a) poly(1-4), and (b) poly(1-6) versus the molar ratio of monomer to initiator ($[M]/[I]$).

Figure 2. GPC traces of (a) poly(1-6) and (b) poly(1-7), including blends. The theoretical and observed (in parentheses) degrees of polymerization (DP) are shown on each trace.

Figure 3. Normalized DSC thermograms of poly(1-6); (a) second heating scan; (b) first cooling scan.

Figure 4 Normalized DSC thermograms of poly(1-7) observed (a) on the second heating, and (b) first cooling scans.

Figure 5. Polarized optical micrograph (magnification 160 \times) of the nematic schlieren texture observed on cooling poly(1-4) 16mer from the isotropic state; 77 °C.

Figure 6. Normalized DSC thermograms of poly(1-5) 9mer and 12mer; (a) second heating scan; (b) first cooling scan.

Figure 7. Dependence of the phase transition temperatures on the GPC determined degree of polymerization of (a) poly(1-2), (b) poly(1-3), (c) poly(1-4), (d) poly(1-5), (e) poly(1-6), (f) poly(1-7), and (g) poly(1-8). All data are from the second heating scans.

Figure 8. Dependence of the phase transition temperatures on the flexible spacer length (n methylenic units) of the 100 mers and 50 mers of poly(1- n).

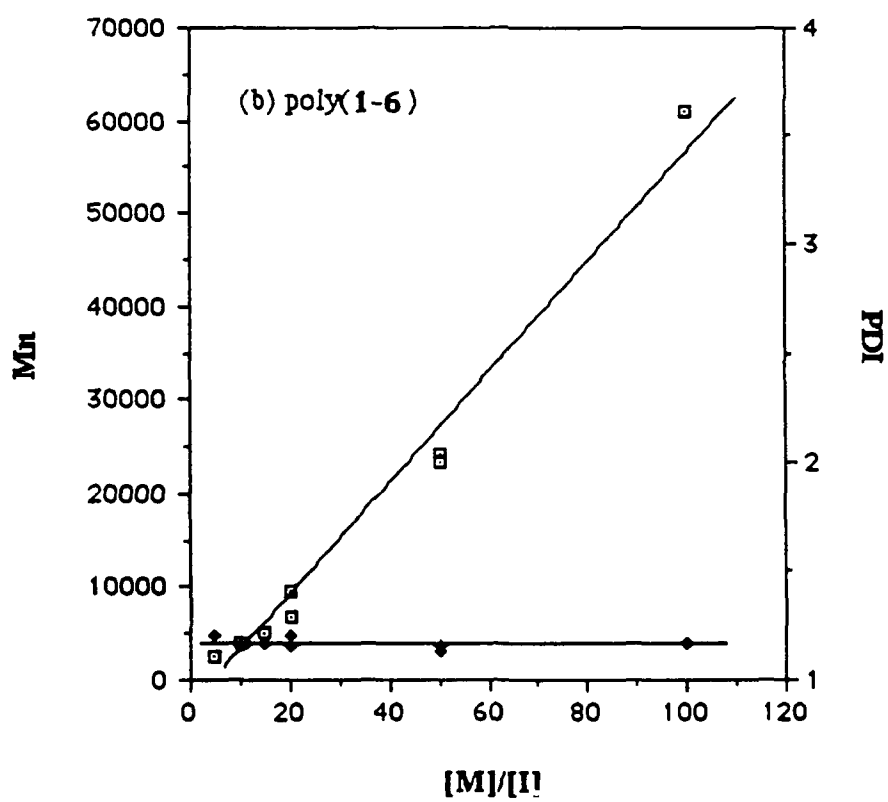
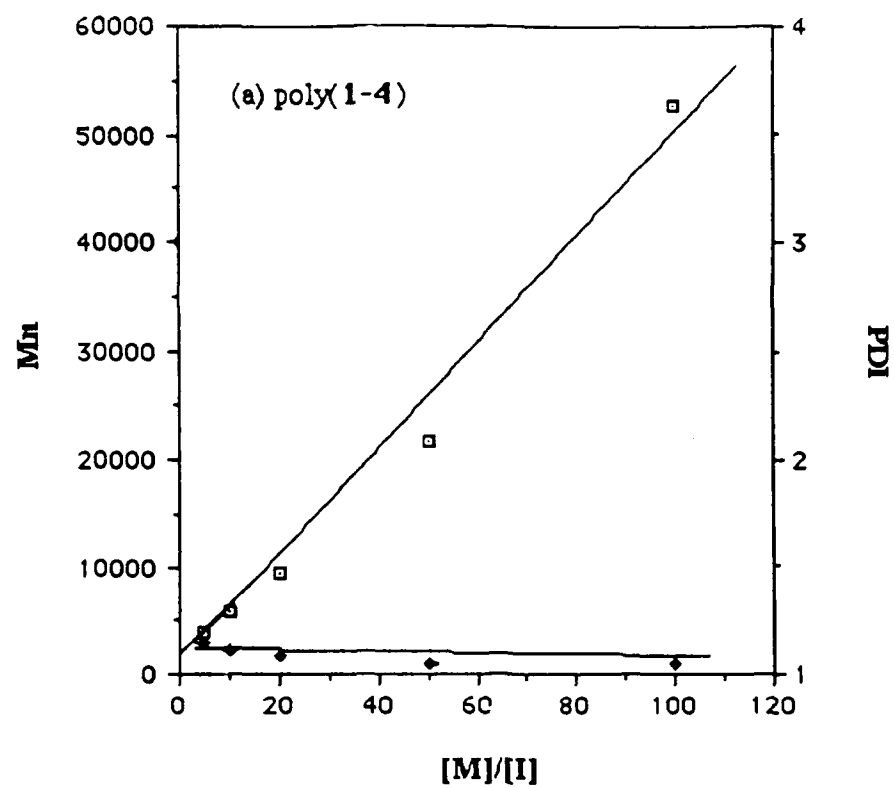


Figure 1.

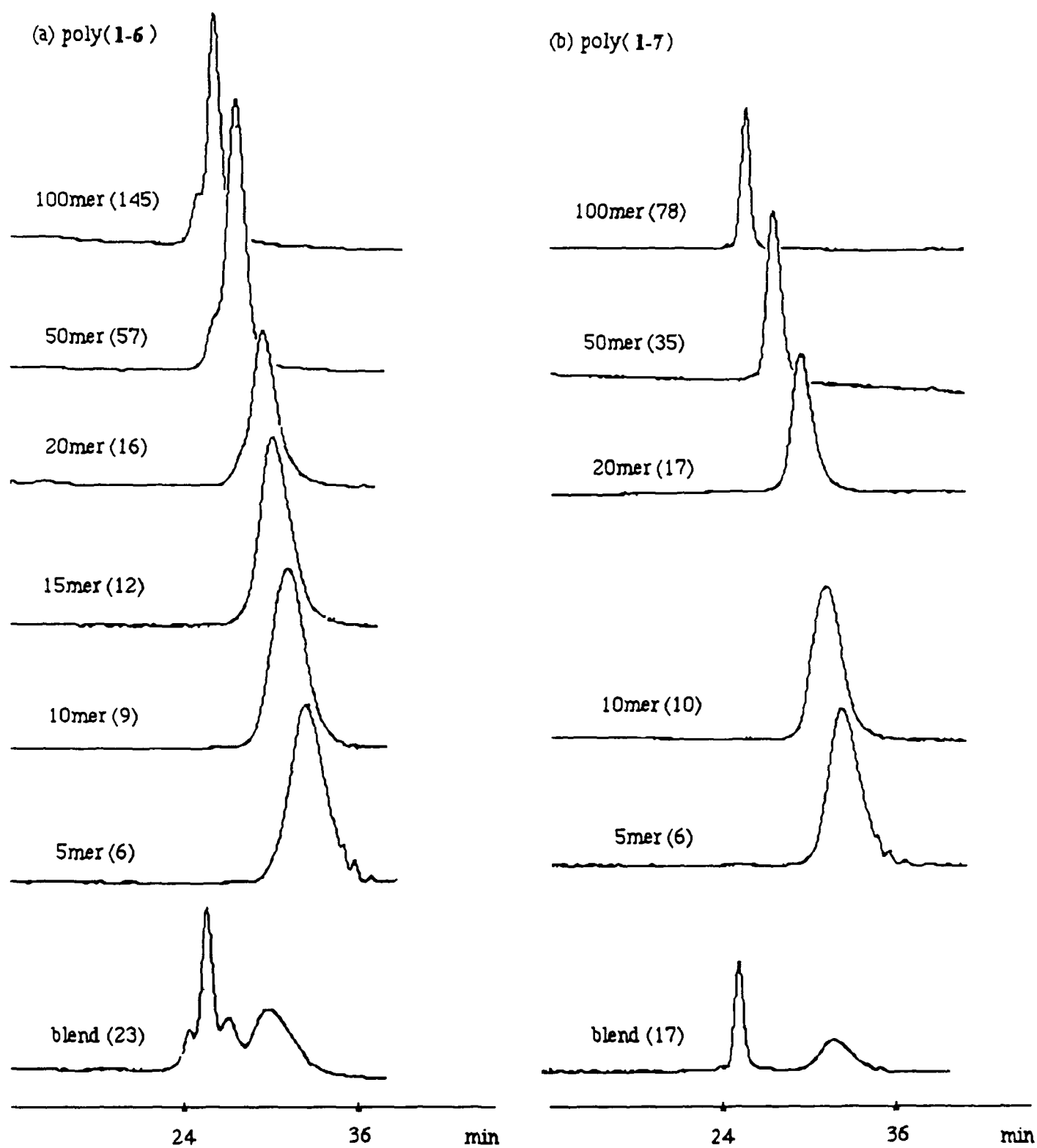


Figure 2. GPC traces of poly(1-6)(a) and poly(1-7)(b).

poly(1-6)

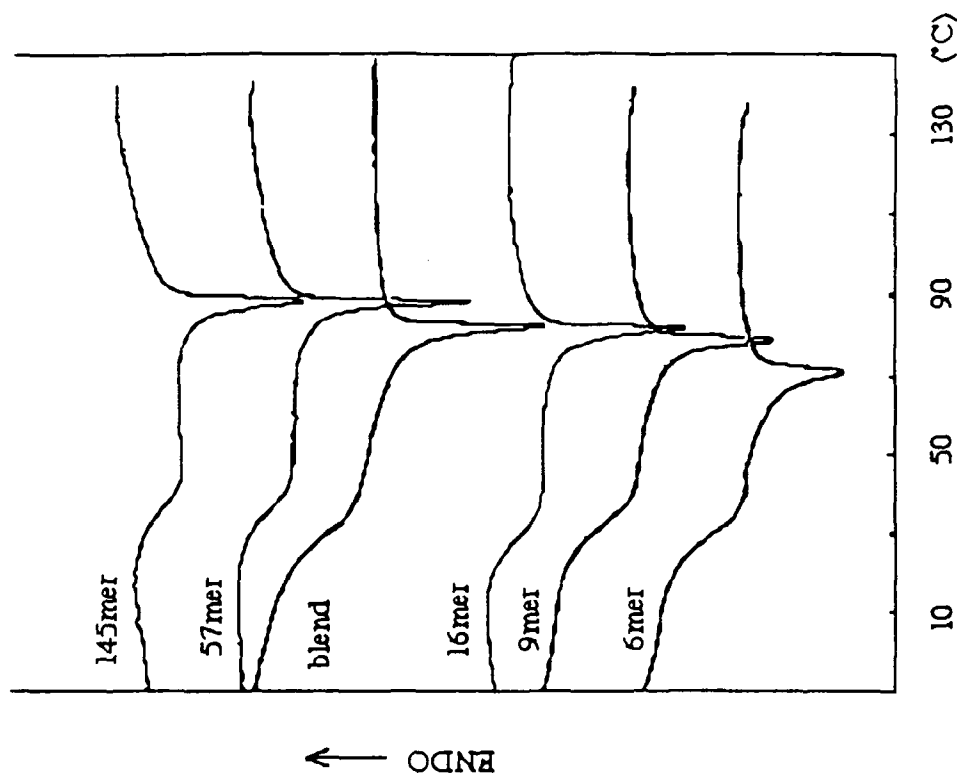
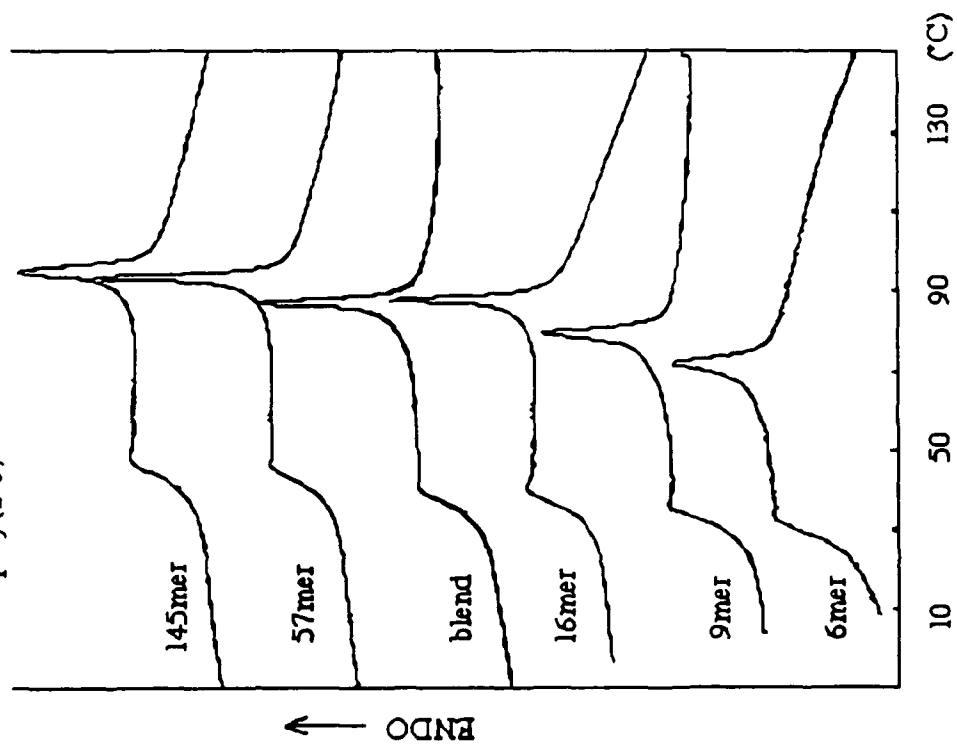


Figure 3

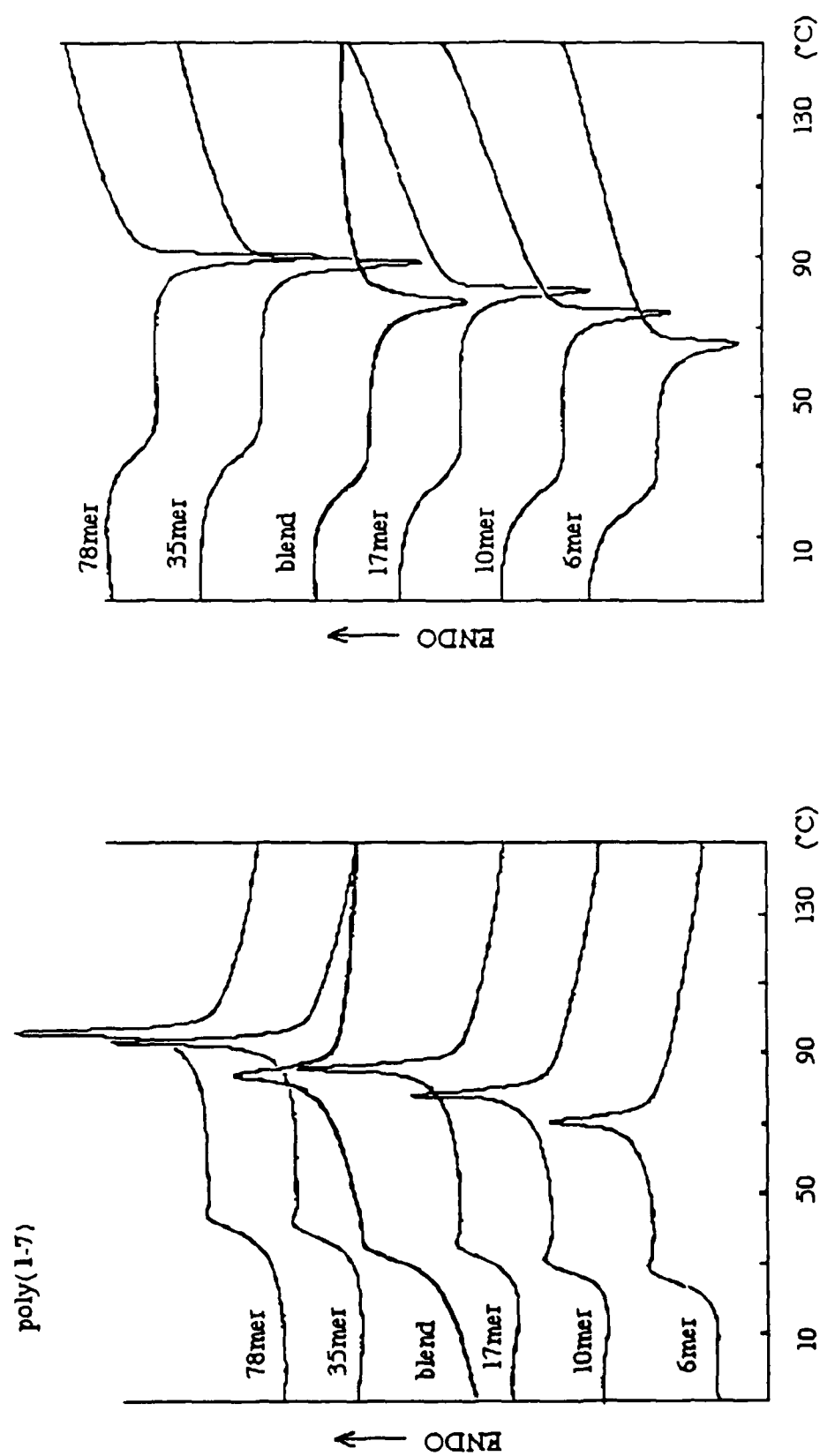


Figure 4



C4. 10mic x 160. 27°C

Figure 1

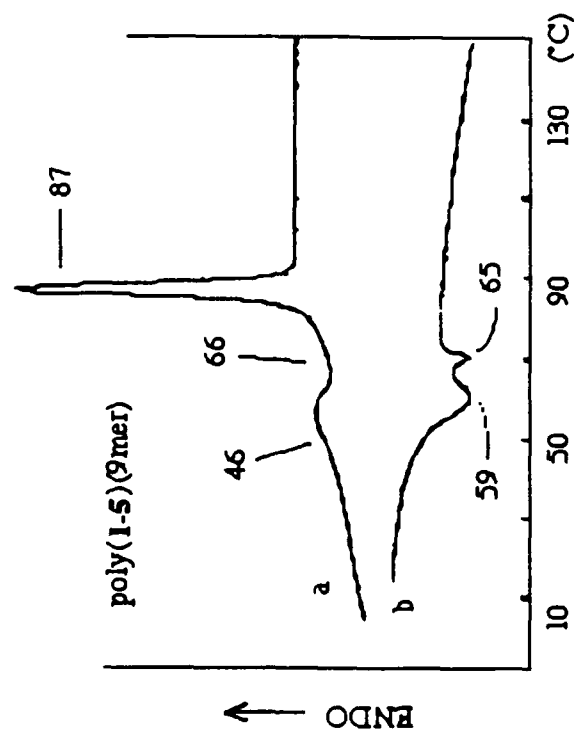
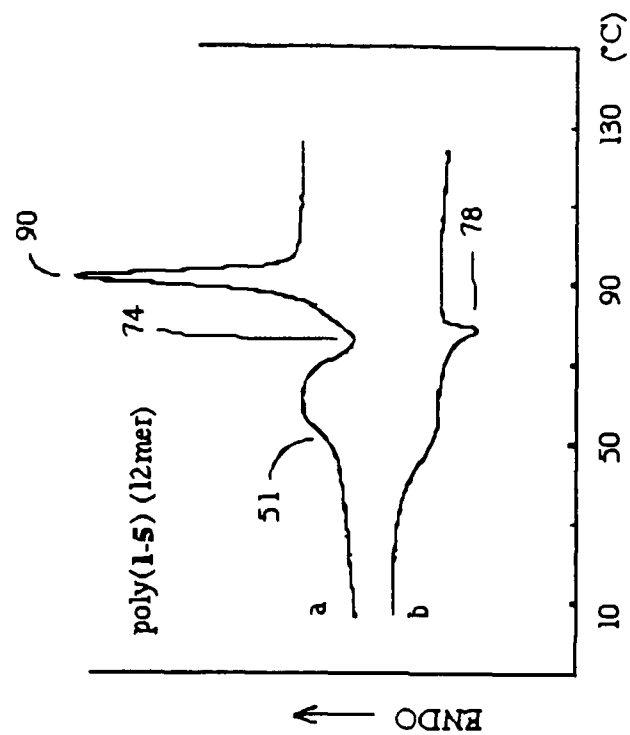


Figure 6.

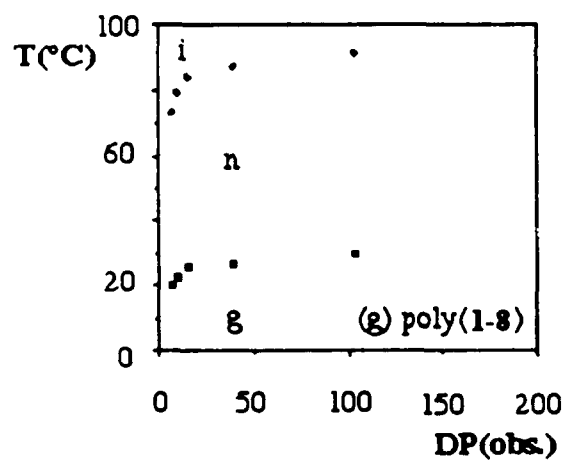
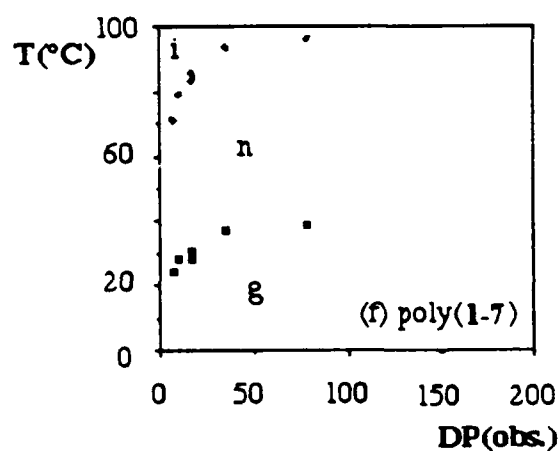
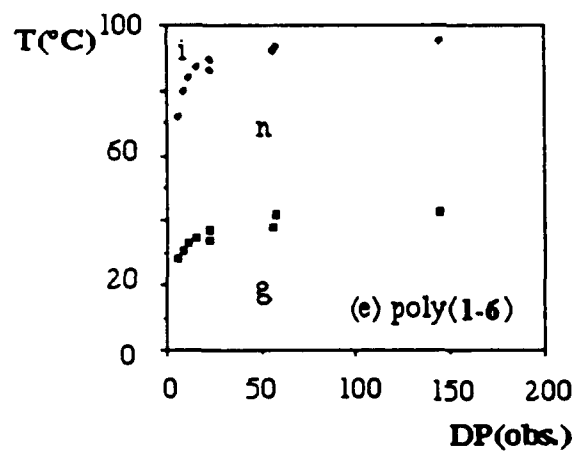
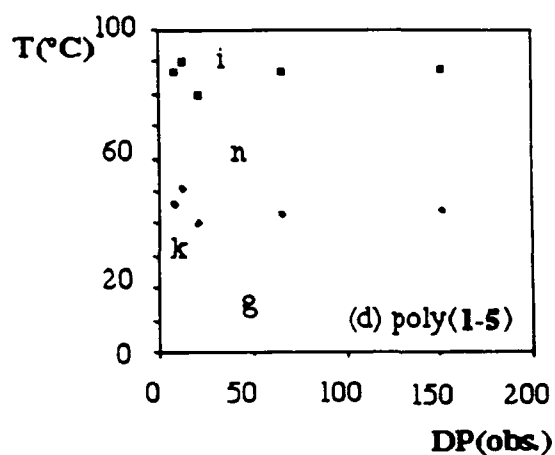
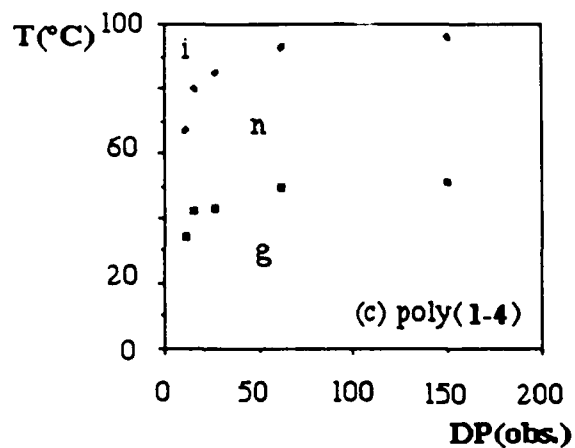
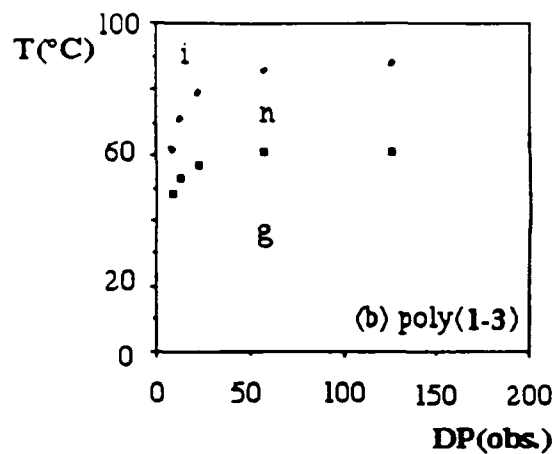
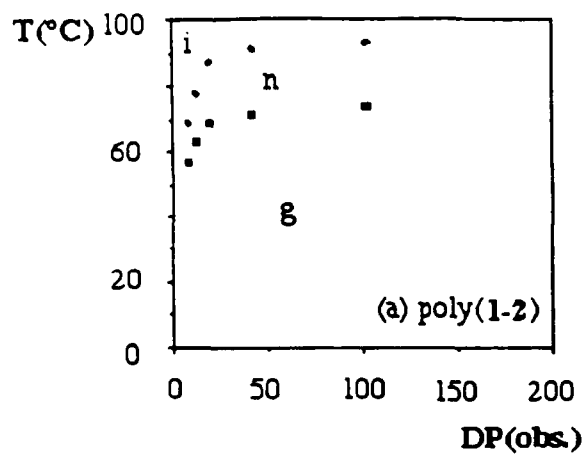


Figure 7.

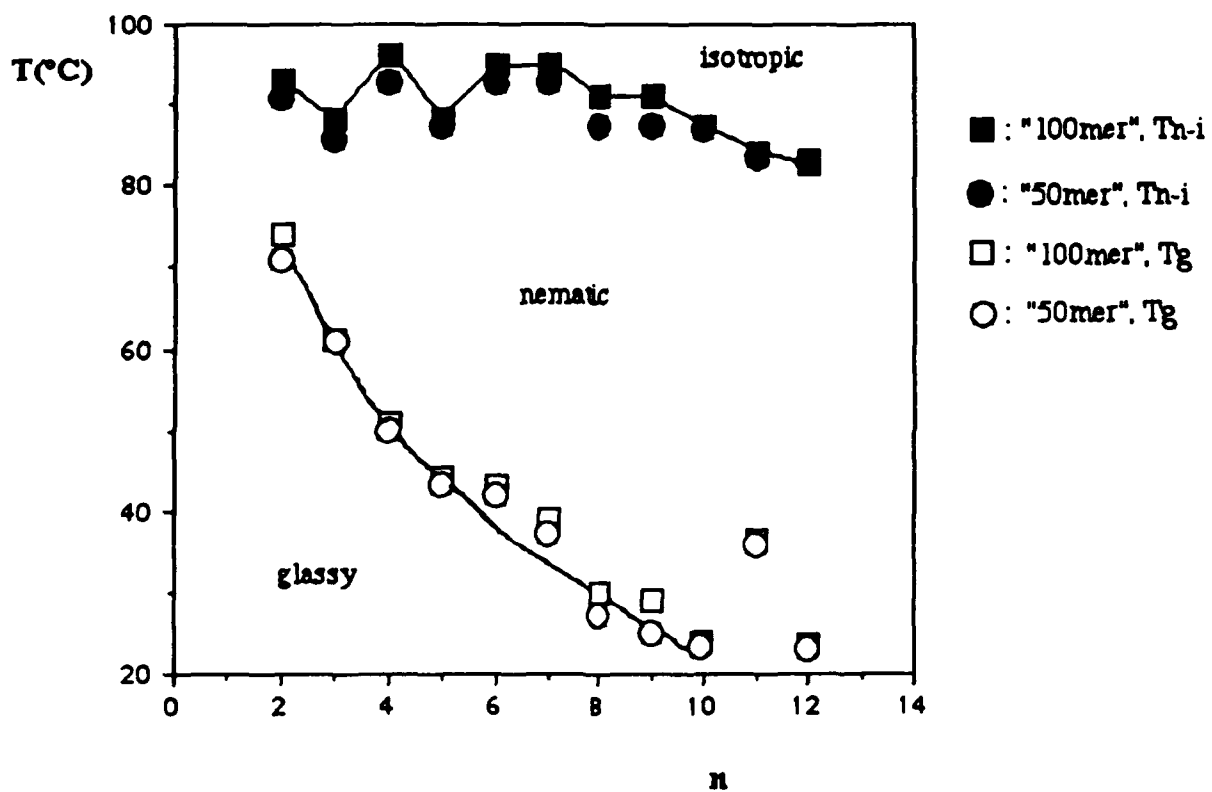


Figure 8.

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